

## **Comment on: "Vibrational Recognition of Hydrogen-Bonded Water Networks on a Metal Surface"**

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68.43.Bc, 68.35.-p, 82.30.Rs

Meng, et al.<sup>1</sup> report ab-initio total-energy and molecular-dynamics calculations for  $\sqrt{3} \times \sqrt{3} R30^\circ$  adsorption layers of H<sub>2</sub>O/Pt(111). Their inference that "theoretical energetics and vibrational dynamics indicate the existence of a well-ordered molecular bilayer on this surface" is unpersuasive for several reasons. One is that the reported bilayer binding energy, 534 meV per H<sub>2</sub>O excluding zero-point energy,<sup>2</sup> is  $\sim 0.2$  eV below the theoretical lattice energy of a water molecule in ice-Ih.<sup>3</sup> Thus, the bilayer is thermodynamically unstable against forming a three-dimensional ice mound. Another is that both He-atom and electron diffraction have shown

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<sup>b</sup> Work supported by the DOE Office of Basic Energy Sciences, Div. of Mat. Sci. and Eng.

<sup>c</sup> SNL is operated by Sandia Corporation, a Lockheed-Martin Company, for the U. S. DOE under Contract No. DE-AC04-94AL85000.

that the wetting layer on Pt(111) has  $\sqrt{39} \times \sqrt{39} R16.1^\circ$  periodicity with 32 water molecules per primitive surface unit cell, not  $\sqrt{3} \times \sqrt{3} R30^\circ$  periodicity with two.<sup>4,5</sup> The reason is that the Pt-Pt distance is too large compared to the lattice constant of ice. In the  $R16.1^\circ$  superlattice, with  $\sim 23\%$  more water molecules per unit area than in a  $\sqrt{3} \times \sqrt{3} R30^\circ$  bilayer, this problem is solved.

Fig. 1 shows a representative “H-down”<sup>6</sup>  $\sqrt{39} \times \sqrt{39} R16.1^\circ$  water adlayer. Note that because of the unit cell's  $16.1^\circ$  rotation, *few O atoms are in atop sites*. Thus, Ref. 1's discussion of atop-site bonding is largely beside the point.<sup>7</sup> More important, the adsorption energy of the optimized structure of Fig. 1 is 0.60 eV<sup>8</sup> (using the VASP computer code<sup>9</sup> as in Ref. 1). Though still  $\sim 0.1$  eV too small to explain why wetting occurs, this energy is 66 meV larger than Meng, et al.'s result, implying that Ref. 1's  $\sqrt{3} \times \sqrt{3} R30^\circ$  bilayer is far from optimal even among 2-d adsorption structures.

To understand why Pt(111) wets, analysis of the  $\sqrt{39} \times \sqrt{39} R16.1^\circ$  structure is unavoidable. Of considerable interest are the energetic

significance of local proton disorder in the R16.1° water adlayer<sup>10</sup> and of the formation of H<sub>3</sub>O<sup>+</sup>- and OH<sup>-</sup>-like surface species. Both are apparent in Fig. 1.

### Figure Caption –

**Fig. 1 - An “H-down”  $\sqrt{39} \times \sqrt{39}$  R16.1° water layer on Pt(111).<sup>6</sup> Top view, with Pt, O and H atoms shown as gray, white and black spheres. Dashed line indicates the surface unit cell. Black and white arrows point to H<sub>3</sub>O<sup>+</sup>- and OH<sup>-</sup>-like adspecies formed as this structure was optimized.**

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<sup>1</sup> S. Meng, et al., Phys. Rev. Lett. **89**, 176104 (2002).

<sup>2</sup> Meng, et al. do not mention zero-point energy. Without including it, I reproduce the energy they report.

<sup>3</sup> P. J. Feibelman, Science **295**, 99(2002), Table I.

<sup>4</sup> A. Glebov, et al., J. Chem. Phys. **106**, 382 (1997).

<sup>5</sup> S. Haq, J. Harnett, A. Hodgson, Surf. Sci. **505**, 171(2002).

<sup>6</sup> “H-down,” means that H atoms not participating in H-bonds have O atoms above them and Pt's below, as in Ref. 1, Fig. 1d.

<sup>7</sup> A similar criticism applies to H. Ogasawara, et al.'s effort to deduce water-adlayer structure from X-ray spectroscopic measurements (see Phys. Rev. Lett. **89**, 276102(2002)). These authors appeal to yet another first-principles

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optimization of a  $\sqrt{3} \times \sqrt{3} R30^\circ$  water layer on Pt(111) adsorption layer data to interpret their spectra.

<sup>8</sup> The optimization was on a 3-layer Pt(111) slab with bottom layer Pt atoms fixed at theoretical bulk Pt-Pt separations. Particulars of the calculation, were as in Ref. 1, but for a larger plane wave basis cutoff, 400 eV, and a surface brillouin zone sample consisting of  $\bar{\Gamma}$  only.

<sup>9</sup> G. Kresse and J. Hafner, Phys. Rev. **B47**, 558 (1993); *ibid.* **B49**, 14251 (1994); G. Kresse and J. Furthmüller, Comput. Mat. Sci. **6**, 15 (1996), Phys. Rev. **B54**, 11169 (1996).

<sup>10</sup> The  $\sqrt{3} \times \sqrt{3} R30^\circ$  bilayer *must* be perfectly proton ordered because there are only two water molecules in its unit cell.

